REMARKS

The issues outstanding in the Office Action mailed May 24, 2004, are the rejections under 35 U.S.C. §§ 112 and 103. Reconsideration of these issues, in view of the following discussion, is respectfully requested. The Examiner is thanked for indicating the withdrawal of the objections to the specification, abstract and claims and the withdrawal of certain rejections under 35 U.S.C. § 112.

Rejections Under 35 U.S.C. §112

The second paragraph rejection of claims 19 and 20 (see paragraph 14 of paper 15) has been repeated. While it is believed that the "+" symbol in claims 19 and 20 would be well understood by one of ordinary skill in the art, the symbol has been replaced with the word it represents. It is evident that the scope of the claim has not been changed by this amendment. Withdrawal of this rejection is therefore respectfully requested.

Claim 9 has also been rejected under the second paragraph in § 112 as a result of the use of the term "blocks" designating the type of polymers (A), (B) and (C). Inasmuch as the term was superfluous, it has been deleted from the claim. Moreover, the claim has been clarified to indicate that it is the parts by weight of the components as stated are based on *the weight* of the triblock copolymer. Inasmuch as the parts "by weight" are previously indicated in the claim, it was believed that it was *the weight* of the triblock copolymer which was clear from the claim. However, in any event, it is submitted that the rejection should now be withdrawn.

Rejections Under 35 U.S.C. § 103

Claims 1, 2, 8 - 11, 13, 15, 16, 18, and 21 - 23 remain rejected under Witschard taken with Rober. Reconsideration of this rejection is again respectfully requested. This rejection, relying upon paragraph 15 of paper 15, is built upon the argument that "Witschard teaches that the block copolymer also includes, as a *third comonomer* in minor proportion, vinyl pyridine, acrylonitrile, *a lower alkyl ester of acrylic acid such as methylmethacrylate*, methacrylonitrile or a vinyl carboxylate such as vinyl acetate (column 8, lines 32 - 44 and column 12, lines 32 - 34) and that the block copolymer is a linear triblock copolymer (column 9, lines 18 - 22), where the third comonomers necessarily constitute the third block of the triblock copolymer." (Emphasis added.)

First, it is submitted, to the contrary, that Witschard does *not* disclose a blend of a semi crystalline thermoplastic fluororesin an ABC triblock copolymer, in which the A block is compatible with the fluororesin, the B block is incompatible with the fluororesin and incompatible with the A block, and the C block is incompatible with the fluororesin, the A block and the B block. In fact, the cited portion of Witschard teaches a "block polymer" component with a "major proportion" of monomer units derived from (1) a mono-alkynyl-substituted aromatic compound of the benzene or naphthalene series containing 8 - 20 carbon atoms and (2) a conjugated hydrocarbon alkadiene of 4 to 10 carbon atoms. See column 7, lines 56 - 64. This disclosure, of course, does not encompass present component (A) of the claimed triblock copolymer, blocks which are incompatible with the fluororesin. Since the disclosure of diblock and triblock polymers at column 9 follows on directly to this disclosure, it is submitted that patentees teach the use, as a third block in the triblock polymer, the same incompatible blocks used in the remainder of the disclosure.

This is all the more evident from the fact that the use of a material, for example, an alkyl ester of an acrylate or methacrylate which is polar and thus *compatible* with the fluororesin, requires special handling and techniques which are not disclosed in the patent. In particular, patentees teach that the synthesis of their block copolymers is by anionic polymerization, see column 8, lines 54 - 57. Such chemistry is well known for the production of block copolymers such as styrene/butadienes. When polar monomers such as methacrylates are introduced, it is necessary to lower the reactivity of the anionic sites, or else side reactions occur which result in deactivation of the polymerization. For example, see "Iononic Polymerization Fundamentals", M. Swarc (1996), Section 3.2.3.4, where it is stated that anionic polymerization of acrylic monomers is hampered by side reactions caused by the integral polar groups of these monomers. The authors teach that the interaction of ionic end groups of the propagating polymers with the polar groups of the monomers can terminate the polymerization. The authors further teach that the complex anionic polymerization of methylmethacrylate can be conducted under "special conditions", using specified initiators, solution concentration and reaction temperatures. See also, "Anionic Polymerization: Principles and Practical Applications", H. L. Hsieh (1996), teaching that monomers with polar substituents undergo side reactions with initiators and propagating anions and that polymerization thereof is not always possible. The authors moreover teach that it is necessary to carefully select initiators in order to

conduct such a polymerization, and also that it is necessary to conduct polymerizations at relatively low temperatures.

The polar monomers discussed at column 8, lines 40 - 44 of Witschard thus would be well known to require special anionic polymerization conditions, if they were to be used as a *discrete* block in the preparation of a triblock polymer. However, patentees fail to disclose such special conditions and, as a result, one of ordinary skill in the art would interpret the Witschard disclosure for exactly what it states at column 8, lines 32 - 39: the monomers used in the polymerization might contain small amounts of polar monomer as "comonomer units" but, clearly, not as a discrete block in and above themselves. Thus, where triblock polymers are disclosed by the patent, it is clear that they are triblocks of materials which are incompatible with the fluororesin, and not inclusive of a block which is compatible with the resin as per presently claimed A. This is clearly why the term "minor proportions" is used in the patent inasmuch as one of ordinary skill in the art would understand, if too great a proportion of the material was used, the polymerization would be deactivated. As a result, it is submitted that patentees simply fail to teach the use of an incompatible A block, and thus do not suggest the present claims under 35 U.S.C. §103.

Moreover, patentees do not teach that metharylate esters can be used at all, much less as a discrete block of the polymer. Column 8, lines 32 - 44 and column 12, lines 32 - 34, *argued* to show that patentees teach the use of methylmethacrylate as material qualifying as the presently claimed A block, are being misinterpreted. The Office Action now admits that col. 12, lines 32-34 of the disclosure is cited "only to provide evidence that methylmethacrylate is a lower alkyl ester of acrylic acid." As noted previously, this portion of the patent relates to *organic processing aids*, see line 30. Moreover, methylmethacrylate is *not* a lower alkyl ester of *an acrylic* acid, but rather a lower alkyl ester of *methacrylic* acid. See, for example, *Ullmann's Encyclopedia of Industrial Chemistry*, volume A-16, pages 441 - 442, indicating that it is *methacrylic* acid used to produce methylmethacrylate. The passage at column 12 relied upon by the Office Action to allegedly teach that methylmethacrylate is a lower alkyl ester of acrylic acid does not do so. The entire sentence states as follows states as follows:

> "The organic processing aid contemplated for incorporation into the polyvinyl halide composition is typically a polymer of a lower alkyl ester of acrylic acid or methacrylic acid, e.g., methylmethacrylate."

It is evident that "methylmethacrylate" modifies *methacrylic* acid, not acrylic acid, consistent with the discussion in Ullman's, *supra*. Moreover, it is again emphasized that this portion of the disclosure relates to organic processing aids, and does not teach the use of methylmethacrylate in the block copolymer. Thus, the reference fails to disclose or suggest independent claim 15, requiring the A block to be a homopolymer a copolymer of an alkyl(alkyl)acrylate, much less claim 16, dependent thereon, reciting that the A block is polyprenmethylmethacrylate, i.e., PMMA.

The remaining rejections under 35 U.S.C. §103 are all predicated on the assumption that Witschard teaches a triblock copolymer per the present claims. In view of the foregoing discussion, it is submitted that these rejections should accordingly also be withdrawn.

The claims of the application are submitted to be in condition for allowance. However, should the Examiner have any questions or comments, he is cordially invited to telephone the undersigned at the number below.

The Commissioner is hereby authorized to charge any fees associated with this response or credit any overpayment to Deposit Account No. 13-3402.

Respectfully submitted,

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Whenever an ionic species is solvated by polar solvents, then at least one solvent molecule has to be desolvated to allow a reagent molecule to come in contact with it* (a necessary condition for a reaction). Since the solvation of free ion is expected to be more powerful than that of ion pairs, the heat of desolvation, larger for the former than for the latter, could make the apparent activation energy of the studied reaction larger for the free ions than for ion pairs. It is debatable whether this explanation, generally correct, accounts for the phenomenon discussed here. It seems to us that we deal here with a specific interaction of the monomer with the growing polylactone anion, resulting in blocking of the reaction center and preventing, thus, the propagation. Since the solvated ions contribute to the electric conductance but not to the propagation,** and the fraction of the free ions was determined by the conductance, the *computed* propagation constant, k_p, is too low. Moreover, since the degree of solvation increases at low temperature, the calculated, not the genuine, activation energy of the propagation of the supposedly free ions becomes too high.

The proposed complexation explains the apparent higher reactivity of ion pairs than their free ions in the β-lactone system. Additional support for the proposed complexation of the free ions of the growing polymers by their monomer is provided by the apparent increase of k_p with decreasing monomer concentration. For example, the apparent k_p is $19\ M^{-1}s^{-1}$ when determined at −15 °C for [M] = 3 M, but increases to $490\ M^{-1}s^{-1}$ when [M] decreases to 1 M.***

The point of intersection of the respective Arrhenius lines has no theoretical significance since the value of the apparent k_p depends on the arbitrary choice of the monomer concentration.

The behavior of this system provides a good illustration of the phenomenon observed frequently in cationic polymerization discussed by Plesch [336] (see p. 78).

3.2.3.4 Polymerization of Acrylic Monomers

Understanding of the mechanism of anionic polymerization of acrylic monomers has been hampered by the side reactions caused by the polar groups which are integral components of these monomers. The early studies of these reactions, reviewed by Bywater [307], suffered from an unfortunate choice of experimental conditions: the use of alkyllithium

* Penczek invoked a more specific condition, stressing a less polar transition state of the propagation than of its initial state, resulting in a reduced degree of its solvation compared to the initial state.

** The reactivity of growing polymer ions solvated by their monomer is expected to be high. The solvating monomer should be readily inserted into the polymer chain. If, however, its orientation in the solvation shell is improper for its insertion and its presence hinders the addition of another monomer, the reactivity of the solvated ion might indeed be very low.

*** The much higher dielectric constant of the lactone than of the solvent (CH_2Cl_2) is supposed to account for the preferential solvation by lactone. However, repetition of this study in formamide solvent [338b], a liquid of nearly the same dielectric constant as the lactone, led to similar results, casting doubt on the generality of the discussed phenomenon.

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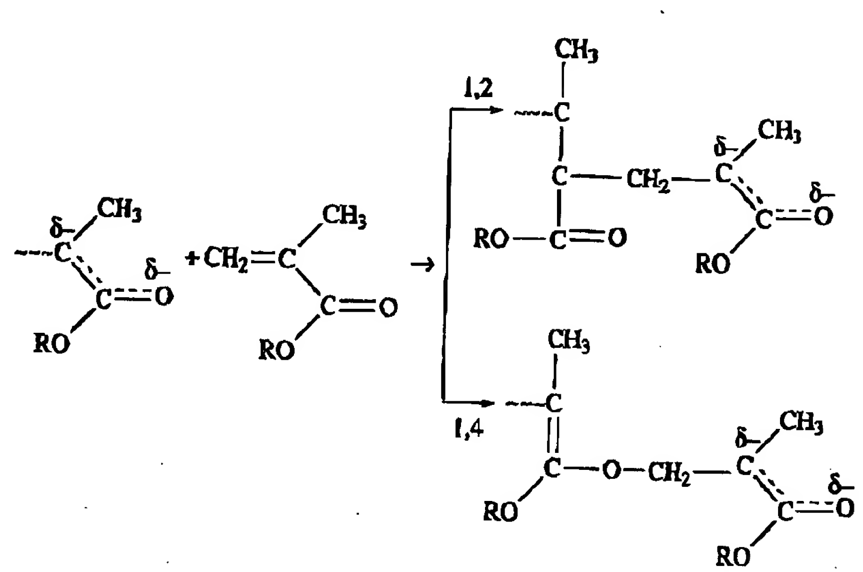
initiators in nonpolar solvents such as toluene. Under these conditions, the interaction of the ionic end groups of the propagating polymers with the polar groups of the monomers terminates the polymerization by a process yielding methoxide salts.

Anionic polymerization of methyl methacrylate is the most extensively investigated polymerization of acrylic monomers, and therefore the results of its study are the main topic of this section.

The anionic polymerization of methyl methacrylate free of termination and chain transfer was first reported by Figueruelo [308], who initiated the reaction by electron transfer in THF or DME at −78 °C. His findings were soon confirmed and extended by Mita et al. [309] and by Lohr and Schulz [310]. The latter, in conjunction with their colleagues, succeeded eventually in producing a polymethyl methacrylate of truly narrow molecular mass distribution.

Anionic polymerization of methyl methacrylate is more complex than the polymerization of styrene, contrary to the early claims [310,313]. Its ideal living nature is revealed only under special conditions: when the reaction is induced by monovalent initiators associated with large cations (e.g., by cumyl cesium) in polar solvents (e.g., DME or THF) at temperatures below −60 °C. The propagation must proceed in dilute solutions containing salts that suppress the participation of free ions in the polymerization.

As emphasized by Müller [311], methacrylates and related monomers (acrylates, acrylonitrile, vinyl ketone, etc.) are bidentate species, and their polar groups compete with the vinyl moieties for the reagents. Hence, the ionic end groups of growing polymers may attack these monomers in two distinct ways, as follows [311]:



Further studies, however, raised doubt about the reality of the 1-4 addition.

The association of the growing polymer end groups, a phenomenon common among enolates, complicates these reactions still further. It leads to the formation of rings when the polymerization is initiated by bifunctional initiators [312,315,318]:

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H. L Hsieh

limitation on the polymerizability of monomers. The distinguishing factor for monomer polymerizability is the mechanism of polymerization. Thus, for anionic polymerizability it is generally considered that there must be substituents on the double bond that can stabilize the negative charge that develops in the transition state for the monomer addition step as shown in Eq. 5.1. These substituents must

$$R^{\ominus} + CH_2{=}C(X)(Y) \longrightarrow \left[\overset{-\delta}{R}\cdots CH_2 \cdots \overset{-\delta}{C}(X)(Y) \right]^{\ddagger} \longrightarrow RCH_2C^{\ominus}(X)(Y) \qquad (5.1)$$

also be stable to the reactive anionic chain ends; thus, relatively acidic, proton-donating groups (e.g. amino, hydroxyl, carboxyl, acetylene functional groups) or strongly electrophilic functional groups that react with bases and nucleophiles [8] must not be present or must be protected by conversion to a suitable derivative [16]. In general, substituents that stabilize negative charge by anionic charge delocalization are the substituents that render vinyl monomers polymerizable by an anionic mechanism. Such substituents include aromatic rings, double bonds, as well as carbonyl, ester, cyano, sulfoxide, sulfone, and nitro groups (see Chapter 2). The corresponding classes of polymerizable monomers are shown in Table 5.1. The general types of heterocyclic monomers that can be polymerized anionically are listed in Table 5.2 (see Chapter 24). The ability to polymerize the corresponding deuterated monomers should also be noted; deuterated polymers are useful for small-angle neutron-scattering investigations of chain conformations in solution and chain dynamics [17]. The range of monomers that can be polymerized anionically without the incursion of termination and transfer reactions includes styrenes, dienes, methacrylates, epoxides, episulfides, cyclic siloxanes and lactones [13,17–22].

Monomers with polar substituents such as carbonyl, cyano, and nitro groups often undergo side reactions with initiators and propagating anions; therefore, controlled polymerization to provide high-molecular-weight polymers is not always possible. Even though some termination reactions occur with certain monomers, especially those with polar functionalities, they can be used to prepare the last-formed block in a sequence. Under these circumstances, control of variables such as molecular weight and molecular weight distribution will be lost. The types of monomers that have been polymerized anionically, but that do not produce living, stable, carbanionic chain ends, include acrylonitriles, cyanoacrylates, propylene oxide, acrolein, vinyl ketones, vinyl sulfones, vinyl sulfoxides, vinyl silanes, halogenated monomers, ketenes, nitroalkenes, and isocyanates [18,19, 21,22].

It is noteworthy and unexpected that the simplest vinyl monomer, ethylene, can be polymerized by an anionic mechanism [18,23–27]. Although the propagating primary carbanion in ethylene polymerization would not be expected to be

stable relative to the substituted carbanions corresponding to the other monomers listed in Table 5.1, the conversion of a double bond to two single bonds provides the energetic driving force for this reaction.

An important aspect of monomer reactivity in anionic polymerization is the relationship among monomer reactivity, the stability of the corresponding propagating carbanionic species, and the appropriate initiating species. It is satisfying to note that there appears to be a general relationship between monomer reactivity in anionic polymerization and the stability of the anions formed by nucleophilic addition or ring opening as deduced from the pK_a values for the conjugate acids of these anions. Thus, the monomers that form the least stable anions (i.e., have the largest values of pK_a for the corresponding conjugate acids) are the least reactive monomers in anionic polymerization; in turn, these less reactive monomers require the use of the most reactive, organometallic initiators as shown in Table 5.3. In general, an appropriate initiator is an anionic species that has a reactivity similar to the propagating carbanionic species [17]. If the initiator is too reactive, side reactions are promoted. If the initiator is relatively unreactive, the initiation reaction may be slow or inefficient.

Similar considerations should be kept in mind for block copolymer synthesis with regard to the reactivity of the polymeric anionic initiator with a second block-forming monomer. Thus, in general, the more reactive propagating anions corresponding to a less reactive monomer group (higher carbanion conjugate acid pK_a) can initiate polymerization of more reactive monomers in a group that forms more stable anions (lower carbanion conjugate acid pK_a), but not vice versa [204]. These relationships are illustrated in Table 5.3, which lists basic monomer types, the pK_a of the conjugate acid of the carbanionic species involved in propagation, and appropriate initiating species for each class of monomers.

B. Monomers with Protected Functional Groups

Functional groups with relatively acidic hydrogens would normally participate in termination or chain transfer reactions in anionic polymerization [17]. These groups can be protected, however, by conversion to suitable derivatives that are stable to the anionic polymerization conditions (initiator and propagating anion) and that can be removed readily after the polymerizations [16,205]. These protected functional groups are listed in section 3.B in Table 5.1. Thus hydroxyl, phenol, and amine functional groups can be protected by conversion to the corresponding silyl derivatives. Mild acid hydrolysis or reaction with fluoride ion in methanol can be used to regenerate the hydroxyl and amine functional groups [16,205]. Aldehyde and ketone functional groups can be protected by conversion to the corresponding imidazolidine, aminal, or acetal derivatives, respectively. The carboxyl functional groups can be protected by conversion to the oxazoline derivative or by use of the hindered *t*-butyl ester. Many of these protecting groups

Table 5.3 Relationships Among Monomer Reactivity, Carbanion Stability, and Suitable Initiators[a]

Monomer Type	pK_a (DMSO)	pK_a (H_2O)	Initiators[b]
Ethylene	56		RLi
Dienes and	44		NR_2^-, RLi,
Styrenes	43		RMt[b], naphthalene radical anions[c], cumyl$^-$ K^+, Mt,
Acrylonitrile	32		RMgX
Alkyl Methacrylates	30–31 (195)	27–28 (195)	Fluorenyl$^-$, Ar_2C^-, ketyl radical anions[d]
Vinyl ketones	26	19 (197)	
Oxiranes	29–32	16–18 (198)	RO^-
Thiiranes	17	12–13 (199)	
Nitroalkenes	17	10–14 (200)	
Siloxanes		10–14 (201, 202)	RO^-, OH^-
Lactones	12	4–5 (203)	RCO_2^-
Cyanoacrylates	11 (196)		HCO_3^-, H_2O
Vinylidene cyanide	11	11 (196)	

[a]pKa values refer to the conjugate acid of the anionic propagating intermediate. pK_a values in DMSO are from Ref. 194 unless noted in parentheses after the number. The references for pK_a values in H_2O are listed in parentheses after the number.
[b]Mt refers generally to alkali metals (Li, Na, K, Rb, Cs).
[c]For example, naphthalene radical anion $\cdot^-$ (Li^+, Na^+, K^+).
[d]$Ar_2CO\cdot^-$.

are themselves not stable to initiators or carbanionic propagating species and require the use of low temperatures for their controlled polymerization [16,205].

C. Styrene Monomers

Styrene monomers are important for living anionic polymerization and many commercial polymers. They can be polymerized in hydrocarbon or polar aprotic media. The ability to polymerize styrenes with both aromatic and side-chain substituents provides routes to polymers with either hydrophobic or hydrophilic character. In addition, the use of protecting groups for reactive functional groups provides an even wider range of functionalized polystyrenes, as shown in Table 5.1.

D. Diene Monomers

1,3-Diene monomers represent another important class of monomers for living anionic polymerization and for preparation of many commercial polymers. The microstructure of polydienes can be varied by changing the counterion, solvent,

temperature, and chain end concentration (see Chapter 9). Lithium is unique among the alkali metal counterions in producing high 1,4-polydienes in hydrocarbon media. High 1,4-polydienes and their copolymers generally have low glass transition temperatures and produce good elastomers. The glass transition temperature increases with increasing amounts of side-chain vinyl microstructure (see Chapter 9).

E. Vinylpyridines

Because of the reactivity of the pyridine ring towards nucleophilic attack [8], the selection of an appropriate initiator and reaction conditions is important to effect the successful polymerization of 2-vinylpyridine (see references cited in Table 5.1, section 3.D). Controlled polymerization of 2-vinylpyridine has been effected by addition of lithium chloride at −78°C in tetrahydrofuran (THF) [206]. In general, the anionic polymerization of 4-vinylpyridine is not carried out because the polymer precipitates from solution during the polymerization [207].

F. Alkyl Methacrylates

The proper choice of initiator and reaction conditions is essential for the controlled anionic polymerization of alkyl methacrylates (see Chapter 23). In general, a less reactive initiator such as 1,1-diphenylhexyllithium, formed by the addition of butyllithium to 1,1-diphenylethylene (Eq. 5.2) (see Chapter 6), is an effective

$$BuLi + CH_2{=}C(C_6H_5)_2 \longrightarrow BuCH_2C(C_6H_5)_2Li \tag{5.2}$$

initiator [121,208–212]. More reactive initiators such as butyllithium react with the ester carbonyl group in competition with the Michael addition to the conjugated double bond; less than half of the initiator molecules initiate chain growth [213]. These polymerizations must be carried out at low temperatures (e.g. −78°C), although it has been reported that polymerizations can be carried out at higher temperatures in the presence of lithium chloride [214,215]. It is even possible to effect controlled anionic polymerization of *t*-butyl acrylate in the presence of lithium chloride [127–129] or lithium 2-(2-methoxyethoxy)ethoxide [216] in THF at low temperatures. In addition, the anionic polymerization of *t*-butyl methacrylate can be carried out at room temperature [217]. The solvent has a dramatic effect on the stereochemistry of the polymerization (see Chapter 23). Highly isotactic polymer can be formed in hydrocarbon solvents such as toluene, whereas highly syndiotactic polymer is formed in tetrahydrofuran [218].